

REMARKS

The claims are 6 to 12 and 14 to 33 with claims 13 to 30 being withdrawn from consideration.

Claims 6 and 11 stand rejected under 35 U.S.C. 102(a) as being anticipated by JP2001-064004.

This rejection is respectfully traversed.

JP2001-064004 discloses nanohorn aggregates heated at 380°C.

On the other hand, applicants' paper, (Carbon 41 (2003) 1273-1280, M. Yudasaka et al.), discloses that the products heated at 1200-2000°C are different from the product "as-grown" regarding their structure (Fig. 6) and properties (Fig. 8), and that the products heated at 380°C have the same structure as the product "as-grown", as can be appreciated from the TEM images (Fig. 6, Carbon article vs. Fig. 5, JP2001-064004). Thus, Carbon 41 (2003) 1273-1280, M. Yudasaka et al. and JP2001-064004 show that the products heated at 1200-2000°C are different from the products heated at 380°C.

Consequently, it is apparent that the products heated at 1200-2000°C, as presently claimed, are unobviously and substantially different from the products heated at 380°C.

In Official Action paragraph 4, it is stated that the patentability of a product does not depend on its method of production. This would seem to suggest that applicants may not show that the properties of a product vary with the method of production. However, it is clarified in Official Action paragraph 4 that applicants can come forward with evidence establishing an unobvious difference between the claimed product and the prior art product.

Also see MPEP § 2114 at page 2100-52 which states that the structure applied by the process steps should be considered when assessing the patentability of the product-by-process claims over the prior art.

Since this has been accomplished, it is apparent that the rejection over the JP2001-064004 reference is untenable and should be withdrawn.

Similar comments are applicable with regard to the rejection in claims 6 to 10, 12 and 31 to 33 under 35 U.S.C. 103(a) as being unpatentable over JP2001-036361 in view of JP2001-064004.

No further issues remaining, allowance of this application is respectfully requested.

If the Examiner has any comments or proposals for expediting prosecution, please contact undersigned at the telephone number below.

Respectfully submitted,

Sumio IJIMA et al.

By: Matthew Jacob
Matthew M. Jacob
Registration No. 25,154
Attorney for Applicants

MJ/aas
Washington, D.C. 20006-1021
Telephone (202) 721-8200
Facsimile (202) 721-8250
May 16, 2007

ATTACHMENTS

1. M. Yudasaka et al., "Structure changes of single-wall carbon nanotubes and single-wall carbon nanohorns caused by heat treatment", Carbon, Vol. 41, pages 1273-1280 (2003).



Structure changes of single-wall carbon nanotubes and single-wall carbon nanohorns caused by heat treatment

M. Yudasaka^{a,*}, T. Ichihashi^b, D. Kasuya^c, H. Kataura^d, S. Iijima^{a,b,c}

^aICORP, Japan Science and Technology Cooperation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

^bNEC, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

^cDepartment of Physics, Meijo University, 1-501 Shiogamaguchi, Tenpaku-ku, Nagoya 468-8502, Japan

^dTokyo Metropolitan University, Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Received 4 November 2002; accepted 8 February 2003

Abstract

Raman spectra and transmission electron microscope images showed that diameter enlargement of HiPco, a kind of single-wall carbon nanotube, accompanied by tube-wall corrugation was caused by heat treatment (HT) at 1000 to 1700 °C. Further enlargement accompanied by straightening of the tube walls and incorporation of carbon fragments within the tubes became obvious after HT at 1800 to 1900 °C. The transformation of some single-wall carbon nanotubes into multi-wall nanotubes was observed after HT at 2000 °C, and most single-wall tubes were transformed into multi-wall ones by HT at 2400 °C. What influence the Fe contained in the HiPco tubes had on these structure changes was unclear; similar changes were observed in single-wall carbon nanohorns that did not contain any metal. This indicates that thermally induced changes in the structure of single-wall carbon nanotubes can occur without a metal catalyst. Heat treatment increased the integrity of the nanotube-papers, and this increase may have been due to tube-tube interconnections created by HT.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: A. Carbon nanotubes; C. Raman spectroscopy, Transmission electron microscopy (TEM)

1. Introduction

Single-wall carbon nanotubes (SWNTs) [1] coalesce and change to SWNTs with larger diameters—for example, double or triple the original diameters—as a result of heat treatment (HT) at about 1400 °C [2,3]. The coalescence transforms SWNTs to multi-wall carbon nanotubes when the HT temperature is above 2000 °C [4]. The processes of these structure changes have been computer-simulated [5–7].

We studied the thermal coalescence of SWNTs by using HiPco tubes [8] and single-wall carbon nanohorns (SWNHs) [9] because both types of SWNTs are available in large quantities and with high purity. In addition, the HiPco tubes had thin diameters, 1 nm or less, and the SWNHs did not contain any metal catalysts.

In former studies on the coalescence of SWNTs, the

SWNTs were produced by the laser-furnace or arc methods and had diameters larger than 1 nm [2,3]. When these SWNTs were coalesced by HT, the diameters became larger than 2 nm, and the radial breathing modes of their Raman spectra became difficult to observe [3,10]. By using HiPco tubes with small diameters of about 1 nm or less, we ensured the diameters of the coalesced tubes would still be less than 2 nm. Therefore, we could observe the Raman spectra [11], in addition to microscopic observation, to precisely study the changes in structure.

Metals are used as catalysts in the production of SWNTs [1,8,12,13], and subsequently remain in the SWNTs. Complete removal of these metals by purification is difficult: even when nitric acid is used, metal particles protected by a graphite shell cannot be removed. In addition, acid treatment introduces defects and/or chemical modification in the SWNTs [14], and the metal catalysts are likely to influence the thermal coalescence of SWNTs by way of these defects [5]. On the other hand, SWNHs do not contain any metal catalysts [9], so studying thermally induced structure changes of SWNHs allowed us

*Corresponding author. Tel.: +81-29-850-1190; fax: +81-29-850-1366.

E-mail address: yudasaka@frl.cl.nec.co.jp (M. Yudasaka).

to elucidate the coalescence when it was unaffected by metal catalysts.

Thermal coalescence is interesting in that it enables us to enlarge and control the diameters of SWNTs. In addition, we expect coalescence to enable tube–tube connection, which might be useful for increasing the integrity of constructions made of SWNTs. In this study, we show that HT increased the integrity of papers made of HiPco SWNTs or a HiPco–SWNH mixture.

2. Experimental

As-produced HiPco SWNTs were purchased from Carbon Nanotechnologies. SWNHs were formed by CO₂ laser vaporization of graphite without using metal catalysts in a 760 Torr Ar (99.999%) atmosphere [9] (1 Torr=133.3222 Pa). About 10 mg of HiPco tubes and SWNHs were heat treated: when the HT temperature was lower than 2000 °C, HT was carried out in a vacuum of 10⁻⁵ Torr for 5 h, and when the temperature was 2400 °C, HT was done in 760 Torr Ar (99.999%) gas for 2 h. Structure changes in the SWNTs were studied by transmission electron microscopy (TEM) and Raman spectrum measurement.

The thermal stability of the HiPco tubes and their metal content before and after HT were studied by thermogravimetric analysis (TGA) carried out in an oxygen atmosphere (O₂ 1%, Ar 99%) from room temperature to 1000 °C with a temperature elevation rate of 1 °C/min.

To make paper sheets of as-grown HiPco tubes, the HiPco tubes were first mixed with ethanol and filtered. Residues on the filters were then dried and used as HiPco

papers. We also made a mixture of as-grown HiPco tubes and SWNHs with a weight ratio of about 1:1 and formed papers from the mixture in a similar way. The papers were heat-treated and their integrity was checked to see whether the papers were degraded by ultrasonication (150 W) in ethanol for 3 min.

3. Results and discussion

3.1. Structure change of HiPco SWNTs caused by heat treatment

Raman spectra of the as-grown HiPco tubes measured with an excitation wavelength of 488 nm showed five radial breathing modes (RBMs): peaks (a) to (e) in Fig. 1. From the peak positions, the SWNT diameters were estimated [15,16] to be 0.80 (a), 0.94 (b), 1.0 (c), 1.07 (d), and 1.19 nm (e). The RBM-peak positions were not changed by HT when the temperature was at or below 1400 °C (Fig. 1), peak (a) disappeared after HT at 1650 °C, and peaks (b) to (d) became almost invisible after HT at 1650 °C. Peak (e) remained up to HT at 1780 °C (Fig. 1). As the HT temperature increased from 1650 to 1800 °C, new peaks corresponding to larger diameters—1.33 (f) and 1.50 nm (g)—became stronger. After HT at 1900 °C, a weak, broad peak (h) corresponding to about 1.7 nm appeared. These results indicate that the HiPco SWNTs with small diameters were enlarged as the HT temperature increased. However, the disappearance of the RBM peaks observed for the as-produced HiPco tubes and the appearance of new peaks observed for the HT HiPco tubes did not occur at the same HT temperature. The same pattern

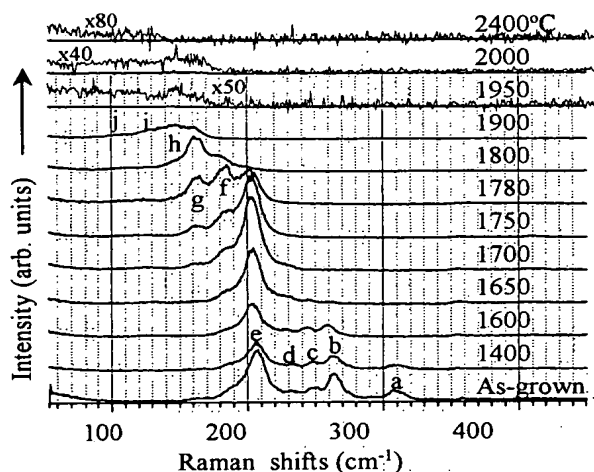


Fig. 1. Radial breathing modes in Raman spectra before and after heat treatment of as-grown HiPco SWNTs. Heat treatment temperatures were as indicated. Diameters estimated from the peak positions are 0.80 (a), 0.94 (b), 1.0 (c), 1.07 (d), 1.19 (e), 1.33 (d), 1.50 (e), 1.68 (f), 1.95 (g), and ~2.2 nm (h).

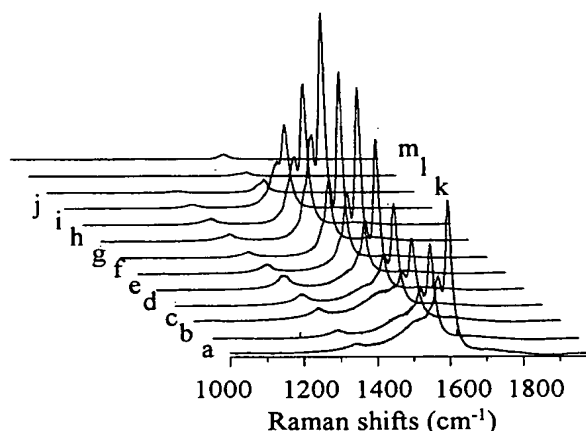


Fig. 2. Tangential modes in Raman spectra of HiPco SWNTs before HT (a) and after HT at 1200 (b), 1400 (c), 1600 (d), 1650 (e), 1700 (f), 1750 (g), 1780 (h), 1800 (i), 1900 (j), 1950 (k), 2000 (l), and 2400 °C (m).

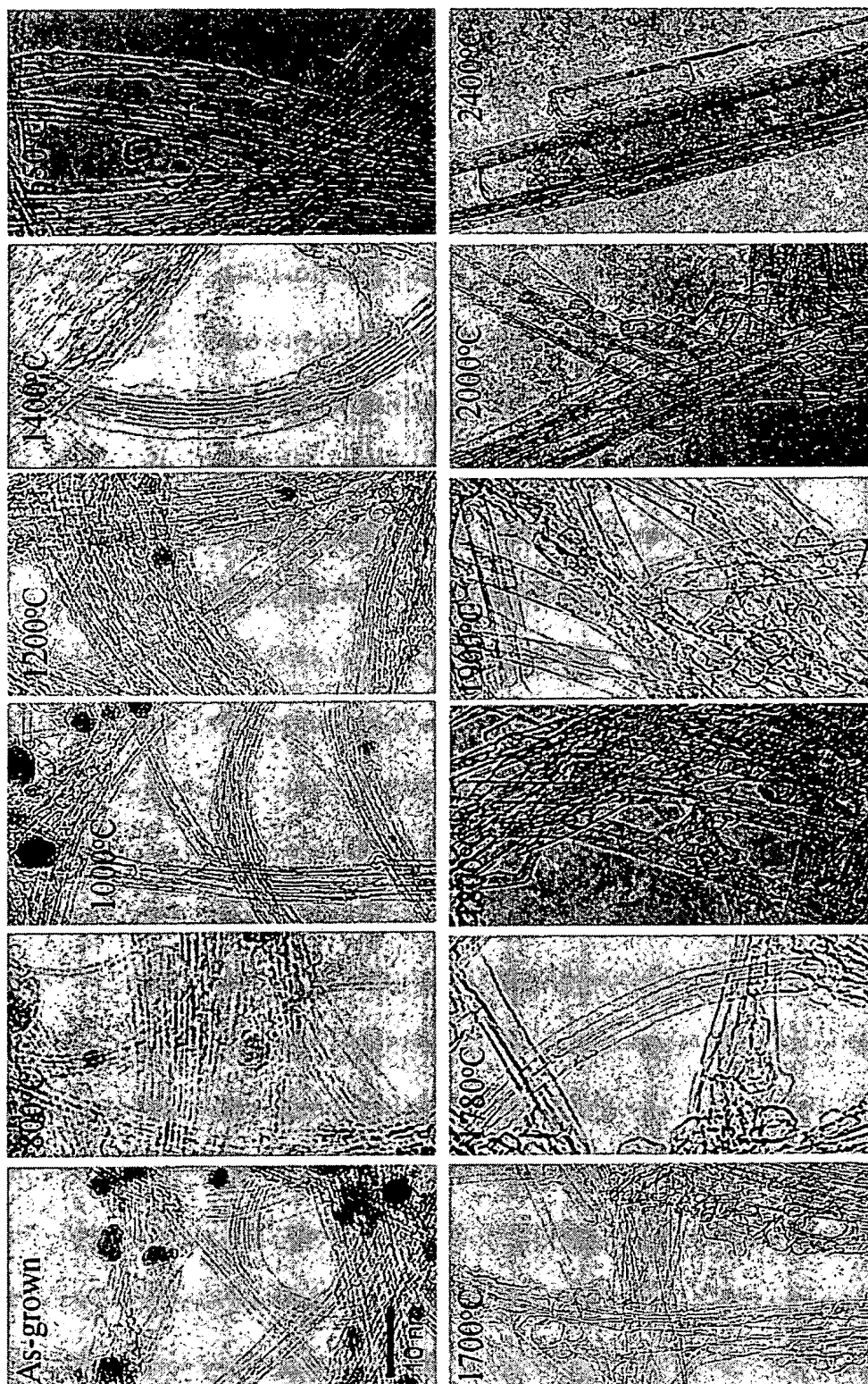


Fig. 3. TEM images of HiPco tubes before and after heat treatment at various temperatures for 5 h.

was observed when a 532-nm excitation wavelength was used for the Raman spectrum measurement (not shown).

Raman spectra of the HiPco SWNTs also showed sharp peaks corresponding to the tangential modes at 1592 and 1565 cm^{-1} and a broad peak corresponding to Fano lines [17,18] at about 1500 cm^{-1} (Fig. 2). Here, the Fano lines are known to be characteristic of metallic SWNTs, and this is consistent with the tight-binding calculation that 488 nm excitation hits the metallic nanotubes selectively in the case of small diameter (~ 1 nm) nanotubes. The Fano lines weakened as the HT temperature increased and disappeared after HT at 1700 $^{\circ}\text{C}$ (Fig. 2f). This is consistent with the disappearance of high-frequency RBM peaks corresponding to the small diameter metallic nanotubes. The peaks of the tangential modes decreased as the HT temperature increased and reached a minimum at about 1400 $^{\circ}\text{C}$ (Fig. 2c). These peaks then increased as the HT temperature rose further and reached a maximum at about 1780 $^{\circ}\text{C}$ (Fig. 2h), but afterwards decreased as the HT took place at higher temperatures (Fig. 2i and j). After HT at 1950 $^{\circ}\text{C}$ or higher, the tangential mode of the SWNTs almost disappeared, and a peak characteristic of graphite

located at 1982 cm^{-1} [19] became the major peak (Fig. 2k–m).

The effect of HT on the structure of the HiPco tubes was also studied with TEM (Fig. 3). TEM observations indicated that the structure of HiPco SWNTs was not greatly changed by HT at 800 $^{\circ}\text{C}$, but the diameters were enlarged and the tube walls became corrugated as a result of HT at 1000 to 1780 $^{\circ}\text{C}$. The tube diameter was further enlarged and the walls straightened by HT at 1800 and 1900 $^{\circ}\text{C}$, though carbonaceous materials were enclosed inside the tubes. Multi-wall carbon nanotubes were observed together with SWNTs after HT at 2000 $^{\circ}\text{C}$. Almost all the SWNTs were transformed to MWNTs when the HT temperature was 2400 $^{\circ}\text{C}$. The interiors of these MWNTs often contained carbonaceous materials, and the number of walls and the distances between adjacent walls differed from place to place within the same tube. The diameters estimated from TEM images are shown in Fig. 4. The number of tubes with estimated diameters larger than 1 nm was significant after HT at 1650 $^{\circ}\text{C}$ or lower, which is not consistent with the diameters estimated from the RBMs of the Raman spectra (Fig. 1)

Comparing the Raman spectra (Figs. 1 and 2) with the TEM results (Figs. 3 and 4), HiPco tubes heat-treated at 1400 to 1700 $^{\circ}\text{C}$ had the weak peak-intensity of tangential-modes in Raman spectra and exhibited the corrugation of the tube walls in TEM images. Raman spectra of these tubes did not show the RBM peaks corresponding to the enlarged diameters. We think that the corrugation of the tube walls reflect the transient structure of tubes in the diameter enlargement or inter-tube coalescing and that the not-uniform diameters hindered Raman-active vibration of the tangential modes and the radial-breathing modes.

This corrugation and the other phenomena, such as the

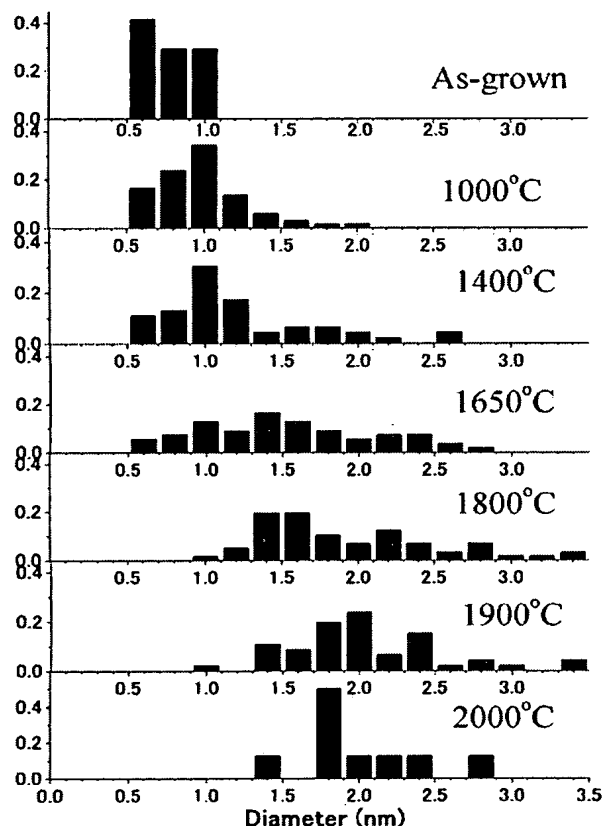


Fig. 4. Diameters distribution of HiPco tubes estimated from TEM images.

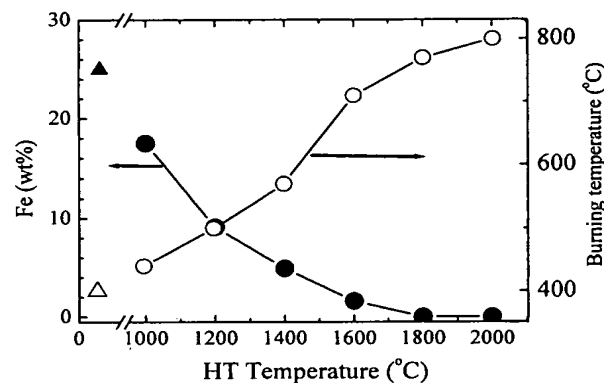


Fig. 5. Quantities of Fe contained and burning temperatures of HiPco tubes before and after HT. Quantities of Fe were estimated from the quantities of TGA residue that remained at 1000 $^{\circ}\text{C}$ by assuming that the residues were Fe_2O_3 . The burning temperatures were the peaks of derivative curves of the weight-loss curves measured in Ar containing 1% O_2 .

carbonaceous materials enclosed within the diameter-enlarged SWNTs and MWNTs and the MWNTs not having uniform adjacent wall–wall distance and wall numbers, indicate that the diameter enlargement accompanies a complex reconstruction of SWNTs. Apparently, as these results show, the process of SWNT-diameter enlargement or that of single- to multi-wall transformation is more complicated than predicted in computer simulations [5,6], where diameter enlargement by coalescence is not accompanied by the tube–wall corrugation or the incorporation of carbon fragments, and multi-wall nanotubes are formed from SWNT bundles having an equal number of walls in individual tubes with no carbon fragments incorporated within the tubes.

The effect of HT on HiPco tubes was also studied by TGA: the burning temperatures of the HiPco tubes and the quantity of Fe are shown in Fig. 5. Here the weight of Fe was estimated from the quantities of TGA residues that were reddish powders. Assuming that all these residues were Fe_2O_3 , the quantity of Fe in the as-grown HiPco tubes was estimated to be about 25% by weight. The Fe

quantity contained in the heat-treated HiPco tubes decreased monotonously with the HT temperature (Fig. 5), and became almost zero after HT above 1800 °C. There was no TGA-residue for HiPco tubes heat-treated at and above 1800 °C. Thus, we think that the structure changes in the HiPco tubes were not influenced by Fe when HT was done at 1800 °C or higher, but we cannot exclude the possibility that Fe affected the structure changes when HT was done below 1800 °C. The burning temperature of the as-grown HiPco tubes was about 400 °C. This is much lower than the burning temperature of about 700–800 °C estimated from the same TGA measurement for SWNTs obtained by laser ablation and purified using nitric acid and oxygen gas [20]. After HT at 2000 °C, the burning temperature became about 800 °C. Here, the burning temperature was determined as the maximum of the derivation curve of the weight loss vs. temperature curve. It is unclear whether the low burning temperatures of the as-grown HiPco tubes and the HiPco tubes heat-treated at lower temperatures were due to the thin diameters, or Fe, or something else.

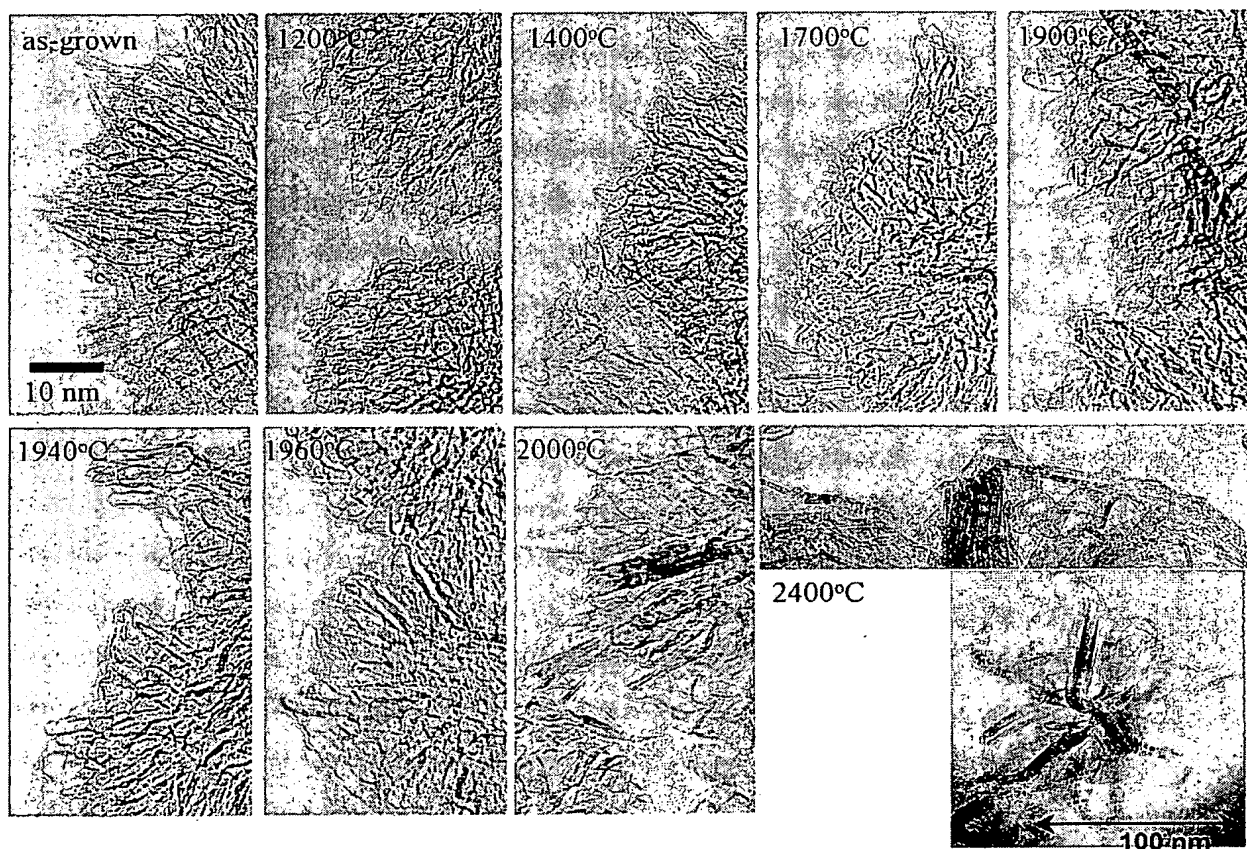


Fig. 6. TEM images of SWNHs before and after HT at various temperatures for 5 h.

3.2. Structure change of SWNHs caused by heat treatment

The structure changes in the SWNHs, which do contain any metal catalysts, caused by HT were similar to those of SWNTs described above. SWNHs [9] are made of single-wall graphene sheets, and form nearly-spherical aggregates with diameters of 80 to 100 nm. One end of a SWNH is united near the center of the nearly-spherical aggregate and the other end has horn-shaped tips at the surface of the almost spherical aggregate [9]. The SWNH diameters were 2 to 4 nm and their lengths were 40 to 50 nm [9]. The wall-to-wall distance of adjacent SWNHs was about 0.34 nm [21].

Structure change in the SWNHs became obvious when the HT temperature was 1200 to 1400 °C: the horn-shaped tips became less sharp and the tube walls became corrugated (Fig. 6). The SWNH diameters enlarged as the HT temperature rose (Fig. 6). Double-wall SWNHs were observed when the HT temperature was 1960 °C (Fig. 6). Multi-wall structures that looked more like bags than tubes were observed when the HT temperature was 2000 °C. After HT at 2400 °C, most of the SWNH aggregates transformed to aggregates of multi-wall graphene sheets and had bag-like structures. Since the as-grown SWNH

diameters were large (2 to 4 nm) and not uniform, the individual tubes, the Raman spectra of the as-grown SWNHs did not show the peaks characteristic of SWNTs, but had peaks at about 1993 and 1350 cm^{-1} . The Raman spectra did not change obviously after HT when the temperature was below 1960 °C, but after HT 2000 °C, the spectra exhibited a strong peak at 1582 cm^{-1} and a small peak at 1350 cm^{-1} , which are characteristics of graphite that has small crystalline sizes [19].

The thermally induced structure changes in SWNHs were generally similar to those in HiPco tubes, suggesting that the tubes made of single-graphene sheets changed their structure to release mechanical stress energy caused by a small curvature by enlarging the curvature via corrugation, and further stabilized themselves by forming a multi-layer structure.

3.3. Integrity of nanotube-papers enhanced by thermal coalescence

Thermal coalescence is an effective means of enlarging the diameter of nanotubes [3–6]. We show here that it is also effective for increasing the integrity of nanotube papers through the formation of tube–tube interconnections. Nanotube papers made of as-grown HiPco, as-grown

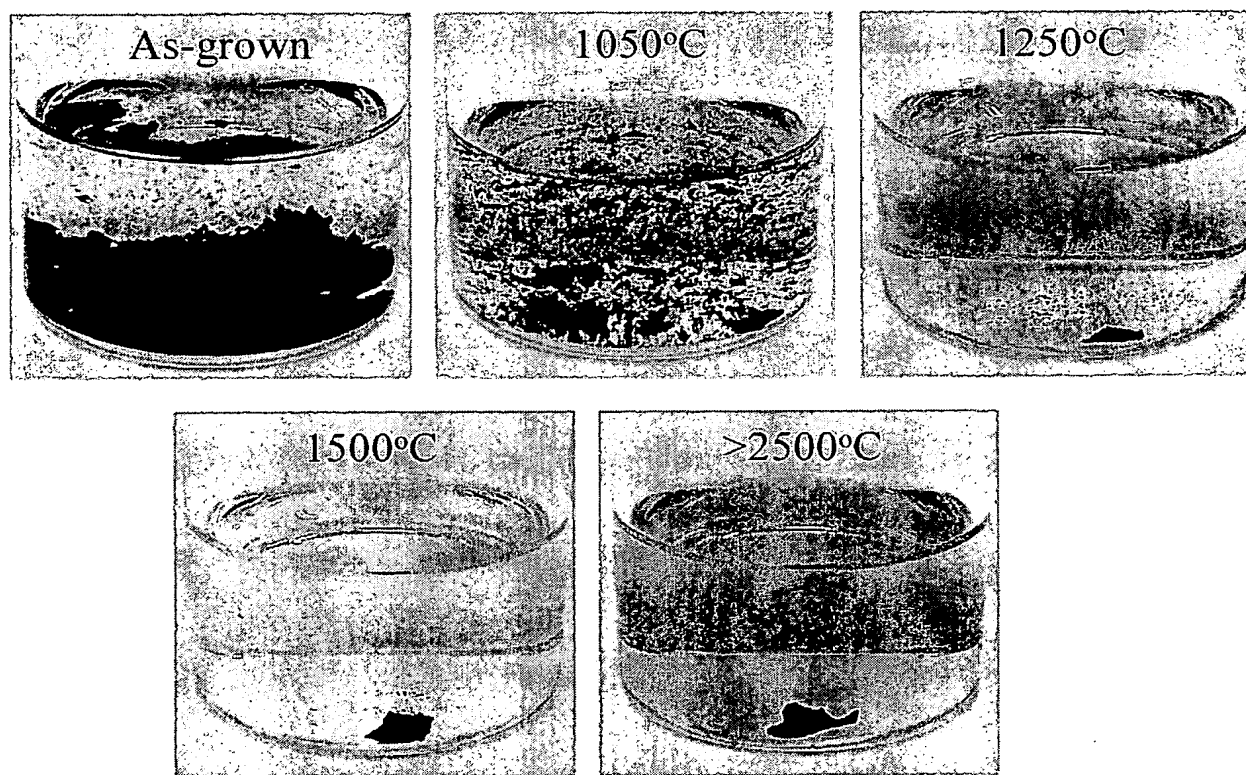


Fig. 7. Photographs of HiPco papers heat-treated at various temperatures after ultrasonic sonication in ethanol.

SWNHs, or mixtures of HiPco and SWNHs with a 1:1 weight ratio (HiPco–NH papers) were heat treated at various temperatures. When HiPco papers were dipped in ethanol and sonicated in an ultrasonic bath (150 W) for 3 min, the papers without HT returned to original powder-like particles that dispersed in the ethanol (Fig. 7). If the HiPco paper was heat treated at 1050 °C, it became resistant to the degradation caused by the ultrasonic turbulence; the level of resistance rose as the HT temperature increased (Fig. 7). The SWNH papers became resistant to the degradation after HT at 2000 °C (Fig. 9). When HiPco–SWNH papers without HT were similarly treated with sonication, they returned to their original particles and dispersed almost homogeneously in the ethanol. This mechanical weakness was not significantly improved by HT at 1050 and 1250 °C. HiPco–NH papers became resistant to the ultrasonic turbulence only after heat treated at 1500 °C or above (Fig. 8).

The HT temperature of 1000 °C needed to increase the integrity of the HiPco papers, corresponded to the tempera-

tures at which the diameter enlargement started (Figs. 3 and 4). This indicates that the greater integrity of HiPco papers after HT was probably caused by the forming of tube–tube interconnections as a result of coalescence. Higher HT-temperatures, for example 2000 °C, were needed to increase the integrity of SWNH papers, perhaps because the spherical forms of the SWNH aggregates led to only a small contact area between the SWNHs belonging to different aggregates. For the HiPco–NH papers, increased integrity became apparent after HT at 1500 °C. This temperature was higher than the temperature range 1200 to 1400 °C, within which the diameter enlargement of the SWNHs started, probably indicating that the HiPco tubes and SWNHs had coalesced.

These results indicate the potential applicability of thermal coalescence to make macroscopic constructions from SWNTs and SWMHs, which may create opportunities to utilize the unique properties of SWNTs and SWNHs at dimensions typical of ordinary day-to-day living.

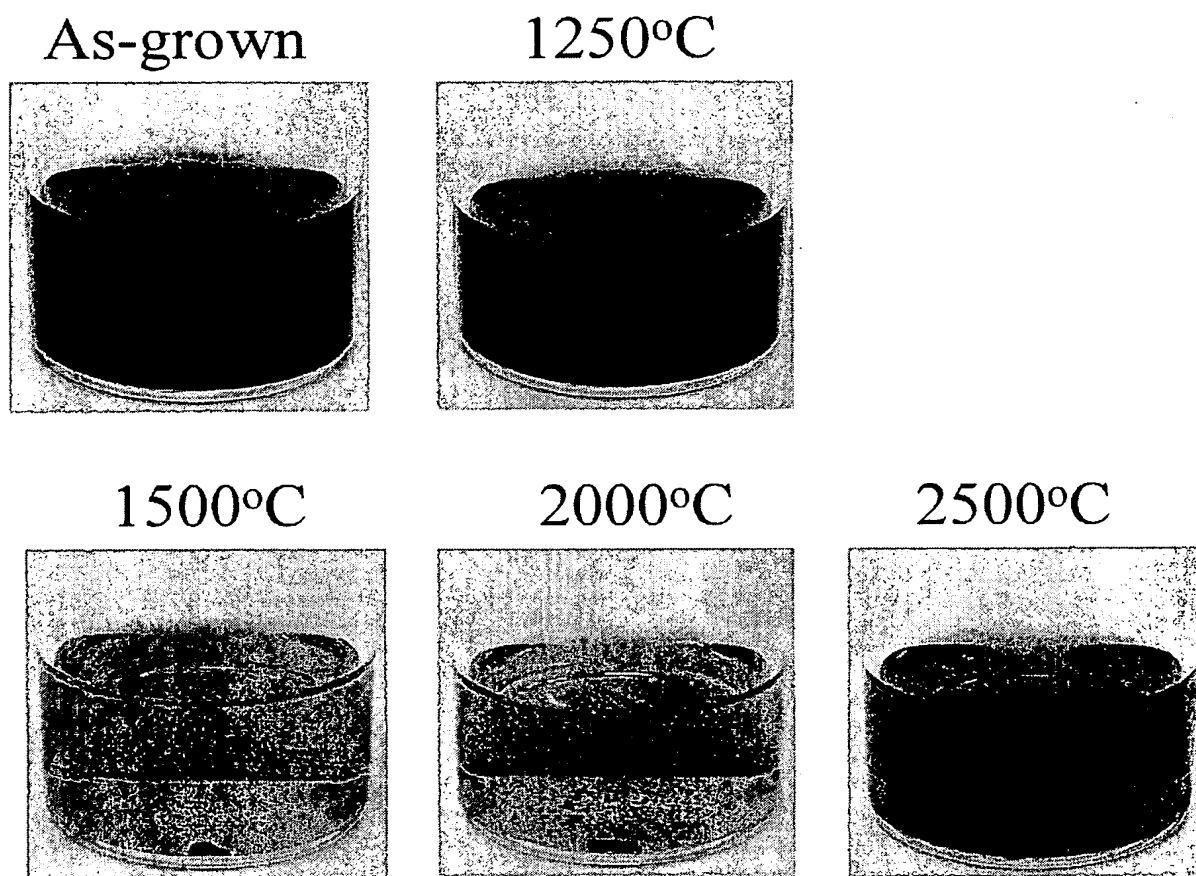


Fig. 8. Photographs of SWNH papers heat-treated at various temperatures after ultrasonic sonication in ethanol.

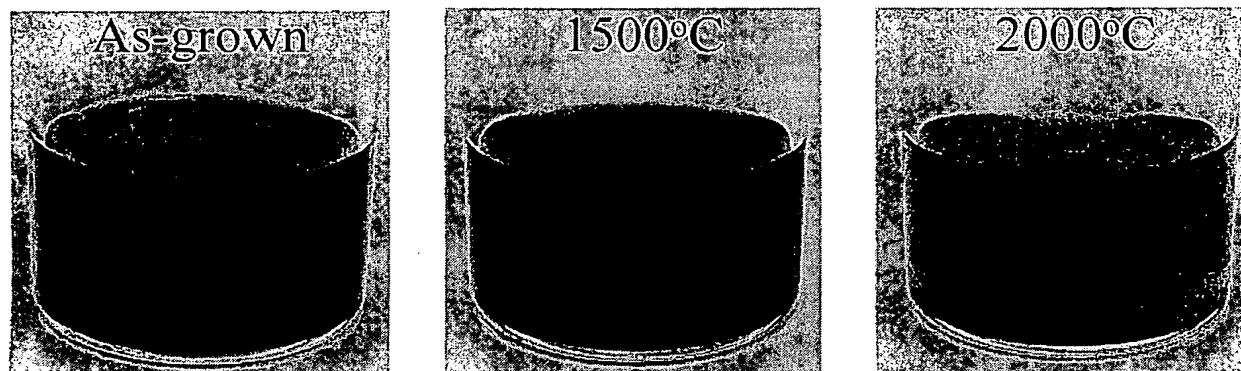


Fig. 9. Photographs of HiPco-SWNH papers heat-treated at various temperatures after ultrasonic sonication in ethanol.

4. Summary

We have studied the detailed changes in the structure of HiPco and SWNH tubes caused by heat treatment. In both materials, diameter enlargement, tube-wall corrugation, and transformation to a multi-wall structure were observed. These thermally induced structure changes are characteristic of the single-wall carbon nanotubes, but the influence of Fe on the thermally induced structure change of HiPco tubes was not clear. In the case of HiPco tubes, incorporation of carbon fragments inside the single-wall and multi-wall tubes was observed, but how the fragments formed is unclear. We also showed that the coalescence of single-wall carbon nanotubes increases the integrity of paper sheets made of HiPco tubes, SWNHs, or a HiPco-SWNH mixture. This increased integrity may result from the tube-tube connections that were created by HT.

References

- [1] Iijima S. *Nature* 1991;354:56.
- [2] Nikolaev P, Thess A, Rinzler AG, Colbert D, Smalley RE. *Chem Phys Lett* 1997;266:422.
- [3] Fang SL, Rao AM, Eklund PC, Nikolaev P, Rinzler AG, Smalley RE. *J Mater Res* 1998;13:2405.
- [4] Metenier K, Bonnamy S, Beguin F, Jounet C, Bernier P, lamy de La Chapelle M, et al. *Carbon*, in press.
- [5] Terrones M, Terrones H, Banhart F, Charlier J-C, Ajayan PM. *Science* 2000;288:1226.
- [6] Lopez MJ, Rubio A, Alonso JA, Lefrant S, Metenier K, Bonnamy S. *Phys Rev Lett* 2002;89:255501.
- [7] Kawai T, Miyamoto Y, Sugino O, Koga Y. *Phys Rev Lett* 2002;89:085901-1.
- [8] Nikolaev P, Bronikowski MJ, Bradley RK, Rohmund F, Colbert DT, Smith KA et al. *Chem Phys Lett* 1999;313:91.
- [9] Iijima S, Yudasaka M, Yamada R, Bandow S, Suenaga K, Kokai F et al. *Chem Phys Lett* 1999;309:165.
- [10] Richter E, Subbaswamy KR. *Phys Rev Lett* 1997;79:2738.
- [11] Yudasaka M, Kataura H, Ichihashi T, Qin L-C, Kar S, Iijima S. *Nano Lett* 2001;9:487.
- [12] Guo T, Nikolaev P, Thess A, Colbert DT, Smalley RE. *Chem Phys Lett* 1995;243:49.
- [13] Journet C, Maser WK, Bernier P, Loiseau A, Chapelle ML, Lefrant S et al. *Nature* 1997;388:756.
- [14] Ebbesen TW, Hiura H, Bisher MA, Treacy MMJ, Shreevekeyer JL, Haushalter RC. *Adv Mater* 1996;8:155.
- [15] Rao AM, Richter E, Bandow S, Chase B, Eklund PC, Williams KA et al. *Science* 1997;275:187.
- [16] Kurti J, Kresse G, Kuzmany H. *Phys Rev B* 1998;58:R8869.
- [17] Kataura H, Kumazawa Y, Maniwa Y, Umezui I, Suzuki S, Ohtsuka Y et al. *Synth Met* 1999;103:2555.
- [18] Rao AM, Eklund PC, Bandow S, Thess A, Smalley RE. *Nature* 1997;388:257.
- [19] Kinoshita K. In: *Carbon, electrochemical and physicochemical properties*, Vol. 3, New York: Wiley, 1988, Chapter 2.2.
- [20] Zhang M, Yudasaka M, Koshio A, Iijima S. *Chem Phys Lett* 2002;364:420.
- [21] Bandow S, Kokai F, Takahashi K, Yudasaka M, Qin L-C, Iijima S. *Chem Phys Lett* 2000;321:514.